California Environmental Protection Agency

Air Resources Board

Engineering and Laboratory Branch
Monitoring and Laboratory Division

MLD SOP ES03

STANDARD OPERATING PROCEDURE FOR THE KARL FISCHER (KF) DETERMINATION OF WATER WITH A KF DRYING OVEN IN CONSUMER PRODUCTS

March 10, 1998, Revision 2

1 INTRODUCTION

In the analysis of consumer products for volatile organic compounds (VOC), the total volatile content of a product is determined by MLD SOP ES01. During this analysis, water in the formulation is included in the total volatile content and must be subtracted from the total volatile content measured gravimetrically (MLD SOP ES01). The percentage of water in consumer products is determined by either a gas chromatographic method (MLD SOP ES04) or by the Karl Fischer (KF) method as described here. This SOP is based on the Karl Fisher procedures specified in ASTM D 4017-88, ASTM D 3742-86 and as modified by this SOP. Water is determined by using pyridine-free Karl Fischer reagent integrated with a drying oven which increases the accuracy and precision of the analysis. Use of trade names or commercial products are examples only, and any equivalent products may be substituted.

2 SUMMARY OF METHOD

The system consists of a Metrohm Titrino Model 720/B10 volumetric KF titrator with an RS232C interface for a balance, printer/computer. A Karl Fischer titration cell with double platinum electrode, 90 and 150 mL vessels with a magnetic stirrer titration stand 703 with pump and a 10 mL "snap-in" buret unit, connected with a Karl Fischer Drying oven 707 with air pump.

The principle of the method involves heating a sample aliquot diluted into 1-methoxy-2-propanol in the oven, where the moisture is carried into the titration vessel by a stream of dry, inert carrier gas (or dried ambient air). The moisture in the titration vessel is titrated continuously until the designated endpoint is reached. Although traditional direct injection sample introduction may be appropriate for some products, the use of the oven provides more consistent and more precise values when interferences are present (see references 8.1 and 8.2).

The traditional Karl Fischer reagent contains iodine, sulfur dioxide in pyridine and methanol. The iodine in the presence of water is reduced to colorless hydrogen iodide. The end point is the appearance of free iodine. The basic reaction of the KF reagent with water is given as:

$$H_2O + SO_2 + I_2 \rightarrow 2\ HI + SO_3$$

New pyridine-free Karl Fischer reagents use amines and glycol ethers to replace the pyridine and methanol.

The method typically involves a dilution of a pre-weighed aliquot of the consumer product in 1-methoxy-2-propanol (MPA). The solvent, MPA, is completely miscible with water forming an azeotrope boiling at 97.5°C. As the water in the sample is heated in the oven it is transferred quantitatively to the titration vessel as the azeotrope, where it is titrated using the pyridine-free KF reagents.

3 INTERFERENCES AND LIMITATIONS

Interferences in the titrimetric water determinations are associated with condensation or oxidation-reduction reactions with a number of substances and compounds. (For more information refer to ASTM E 203 "Standard Test Method for Water Using Karl Fischer Reagent" 1986.)

Use of certain reagents will minimize or eliminate the interferences of many classes of compounds. For example the use of non-methanol containing Karl Fischer reagent and solvent will reduce the interference from aldehydes and ketones. Ammonia and amines can be eliminated by the addition of salicylic acid to the solvent.

Other possible interferences to the KF reagent: certain active metals, metal oxides, metal hydroxides, chromates, melamines, etc.(Ref. 8.1 and 8.2).

4 INSTRUMENTATION AND EQUIPMENT

4.1 Karl Fischer Titration System

4.1.1 Metrohm Titrino 720/B10 Volumetric KF titrator with RS232c interface for balance, printer computer.

4.1.2 A Karl Fischer titration cell with double platinium electrode, 90 and 150 mL vessels, 10 mL "snap-in" buret unit.

4.1.3 Metrohm magnetic stirrer titration stand 703 with pump.

4.1.4 Karl Fischer drying oven 707 with built in air pump and a lab jack stand.

4.1.5 Seiko thermal printer DPU-411.

4.2 Volumetric flask, 10 mL

4.3 Eppendorf pipettor, 250μL and 1.0 mL with pipets

4.4 Hamilton syringes, 50 μL and 250 μL

4.5 Beaker, 100 mL

4.6 Sartorius MC1 analytical balance

4.7 Variable-speed lab vortex/mixer

4.8 Transfer tube/combination pipet

5 REAGENTS AND MATERIALS

5.1 Reagent grade, ASTM Type 1 deionized water, 18.0 MΩ.

5.2 1-Methoxy-2-propanol (Aldrich #26,889-5) stored over 4A molecular sieves.

5.3 Disodium tartrate dihydrate (water content 15.61-15.71%)

5.4 Pyridine-free Karl Fischer titration reagent, Aquastar Comp-5K, 1.0 mL = 5 mg water (EM-AX1698D-1) for aldehydes and ketones.

5.5 Titration solvent, Aquastar Solvent K for use with the Comp-5K (EM-AX1699E-1).

5.6 Salicylic acid, 25 g dried at 110°C, added to the 1.0 L Solvent K bottle for KF analysis.

6 PROCEDURE

The following describes the analysis of water in consumer products using the KF oven.

6.1 KF titer determination (titer calibration) with water, mg water per mL of titrant. Inject directly into the titration vessel 25 μL (25 mg) water and initiate the titration. The titer value is automatically calculated from 3 titrations of the standard and stored as the common variable. This calibration factor is used for subsequent analyses. The KF reagent should be approximately 1 mL per 5 mg water (5.000 mg/mL).

6.2 Change to KF titration method, insert the transfer probe from the KF drying oven into the titration vessel. The oven should be temperature equilibrated to 130°C setting and dry air flowing for at least 30 minutes to allow equilibration.

6.3 A known standard is titrated to check on the operation of the oven. Add 200.0 mg disodium tartrate dihydrate (containing about 15.66 $\pm$ 0.05% water) to the foil boat and initiate the titration. The analysis takes about 10 minutes. Record the results on the procedure Control Chart.

6.4 The percentage of water in the MPA solution (MPA blank) is determined by injecting 250 μL of solvent into a clean foil boat and titrating. The value obtained for the MPA is subtracted from the percentage of water in the sample.

6.5 A control solution of 25% H_2O in MPA is determined. A 1.0 ml aliquot of stock standard is diluted to 10 ml in MPA. Inject 250 μL into the foil boat in the oven. Run the analysis in replicate. The value should be with in $\pm$ 3s of the expected.

6.6 A weighed aliquot of 1.0 mL of the consumer product sample is diluted to 10 mL with MPA. Inject 250 μL into the foil boat in the oven. The analysis is run in replicate, allowing sufficient time between analyzes for the boat to cool. If the boat does not cool to room temperature, loss on the subsequent sample by pre-oven evaporation may occur.

6.7 The amount of water in the sample is calculated by

$$\text{WeightFraction } H_2O = \frac{(\%\ \text{water in dilution} - \%\text{MPA blank})}{\text{grams samplex10}}$$

7 QUALITY CONTROL

7.1 The sensitivity, precision, and accuracy will depend on several factors, particularly the nature of the consumer products material being analyzed.

7.2 All analysis are done in replicate and should have a relative difference of less than ±2%.

7.3 A control chart of the disodium tartrate and the 25% solution is made with the upper and lower control limits set at ±3 s of the historical value. If an analysis is out of the control limits, the conditions are evaluated and the control will be re-analyzed.

7.4 In addition to the tartrate check and the control check a Trip sample of known concentration is run with each sample set.

8 REFERENCES

8.1 ASTM E 203 "Standard Method for Water Using Karl Fischer Reagent" 1986.

8.2 ASTM D 4017 "Standard Test Method for Water in Paints and Paint Materials by Karl Fischer Method" (EPA Method 24).

8.3 Jenkins, V.C., Reilly, Joseph C., Sypowiez, Bob, and Wills, Max T. "VOC Testing Comparison: EPA Method 24 Versus the Cal Poly Method" Journal of Coatings Technology 67(84), 53-59 (1995).

8.4 Metrohm 720 KFS Titrino Instructions for Use. Metrohm 707 KF Oven Instructions for Use.

8.5 Brinkmann Lab, "Karl Fischer Water Determination with the KF Drying Oven" Applications Bulletin No. 109/1e

APPENDIX A

Operation of the Metrohm KF Titrator and KF Drying Oven

1. Turn on the 720 (KF Titrator), the 703 titration vessel (stirbar), the 707 oven and the printer.

2. Check that there is sufficient titrating solution and solvent. The solvent (SOLVENT K) is the most likely one to be replenished and add only when the reservoir is nearly empty. Pour the Solvent K (1.0 L bottle) into the reservoir, to this is added 25.0 g of salicylic acid that has been dried in the oven (for about 1 hr at 110°C) to dehydrate it. (Do not leave the salicylic acid in the oven any longer than necessary, it will sublimate.) With a stirbar in the reservoir bottle, place on a stir plate until the salicylic acid is dissolved.

3. Reposition the replenished reservoir bottle and on the 703 depress the toggle to empty the vessel, then depress the toggle in the front to replenish the vessel with fresh solvent.

4. Turn on the pump on the 707, press PUMP on the front (Note: it may already be on). This operates the air flow that purges the system and transfers the water/MPA azeotrope into the titration vessel.

5. Make certain that the transfer probe from the oven is removed from the titration vessel.

6. Place the single injection plug into the titration vessel. (Note: This shuld be in place, at the end of each analysis set, the oven probe is removed and the injection plug put in place.)

7. On the keypad for the 720, press

   >USER METH
   >RECALL METHOD, ENTER
   >SELECT.....H_2O TITER, ENTER (Note: This should be in place. The titer shuld be re-entered at the end of the analysis.)

   Now should have on the 720 display:

   KFT I (POL) H_2OTiter

8. On the 720, press START to turn COND ON. The system will titrate the background until the display reads: DRIFT OK.

9. Ready to do the water titre. It is absolutely essential to maintain consistency in how the sample is drawn up in the syringe. Using a 50 μL syringe, displace the plunger of the syringe to about 10 μL. Place the tip of the needle into the container of H_2O and draw up the plunger. Observe the meniscus, draw up the water until the bottom of the meniscus is at 24 μL. Remove the

needle and draw the plunger up to be able to read the total amount of solvent in the syringe barrel. You should have 25 μL in the syringe. (Approximately 1 μL is in the needle.)

10. To determine the water titre, press START on the keypad, inject into the titration vessel the 25 μL of deionized water. The display will ask for the SAMPLE WEIGHT, press 0.025, ENTER. This will determine the average mLs of titrant required to titrate the water. The titrant is COMP 5K, where 1.0 mL titrant = 5 mg H_2O. This is run three times (3X) to obtain a statistical average and is automatically entered in the program at C39 as the common variable for the water determination. The water will be titrated to the endpoint and the display will read:

    TITER X.XXXX , e.g., 5.0100

11. On the keypad press.....PRINT, STATISTICS, ENTER. This will give the print out of the 3 injections, show the average and the standard deviation. Record the water titre in the labnotebook.

12. On the 720 press STOP.

    On the keypad: >USER METH
    >RECALL METHOD, ENTER
    >SELECT.....KF, ENTER

    The display will now read: KFT I(POL) KF

13. Drain the vessel, refill with fresh Solvent K and press START on the 720 to turn the COND ON and wait until the displays indicates DRIFTOK.

14. Now ready to use the oven. A clean aluminum foil boat should be in the glass boat inside the insert tube of the oven. Place the transfer probe from the oven into the titration vessel (remove the single injection plug) so the tip of the probe just touches the surface of the solvent in the titration vessel. Press VALVE on the 707, this will switch the valve from purge to transfer. Allow the titration vessel some time to equilibrate, when the DRIFT says OK press the VALVE again so the valve goes back to the purge position.

15. WEEKLY CHECK: Disodium tartrate (15.66% H_2O) is used to check on the operation of the oven. Using tweezers to handle the foil, weigh into a tared foil 200 mg of the disodium tartrate, place the foil into the glass boat and return to the insert tube of the oven and close. (The foils are kept in a desiccator near the KF units.)

    The display on the 707 reads:

    SAMPLE TEMP (130°)
    OVEN TEMP (150°)

Press SELECT, then will display (in place of the OVEN TEMP):
GAS FLOW (100 mL/min)

If the DRIFT on the 720 remains OK, press START on the 707.

16. The 707 has been programmed with a PURGE TIME 30 sec and a COND TIME of 3 sec. The display on the oven will count down the time, when COND=0 sec and the 720 says DRIFT OK, the run will be initiated. The valve will switch from purge to transfer. The boat will move into the oven. On the 720 the display will ask:

    SAMPLE SIZE
    Press, 0.200, ENTER (The weight of the tartrate.)
    UNITS g, ENTER

    Now the titration is on. In the KF program there is an extraction time of 120 seconds to give the oven enough time to heat up sample and start the transfer.

17. On completion of the titration, the boat is moved out of the oven back to the insert tube. The display on the 720 will read:

    WATER XX.XX%

18. The oven will then re-equilibrate and give a peep when the temperature is acceptable and the ready light will come on steadily.

19. Repeat again with a new Al foil to obtain a replicate for the disodium tartrate. When completed, on the keypad press PRINT, STATISTICS, ENTER.

20. The value for the Na tartrate is recorded in the lab notebook and on the QC chart for that instrument. The values should be within the control limits.

21. The oven is used to determine the MPA background water. Insert a new foil in the glass boat and let the system equilibrate as described. Again it is important to be consistent in the manner the sample is drawn in the syringe. In this case and for the samples use a 250 μL syringe (minimum) and measure the amount of sample as described in #9 above. For the blank and the diluted samples 250 μL is used. Inject 250 μL of MPA (this is the MPA that was used to do the dilutions and subsequently carried through out the analysis) into the foil boat. With the DRIFT OK on the 720, press START on the 707 as described above. After PURGE and COND time has elapsed on the 720 the display will ask:

    SAMPLE SIZE Press 0.250, ENTER
    UNITS g, press ENTER

This will start the titration of the MPA with the 120 second extraction delay. Upon completion of the titration the display will read:

WATER X.XX%

22. The MPA background check is run two times, upon completion press PRINT, STATISTICS, ENTER. Record the value in the lab notebook.

23. The background value obtained from the MPA analysis is subtracted from the value for ALL the sample analysis to correct for the MPA solvent dilution.

24. A water check is made as a control for the system. A 25% solution of water in MPA is prepared as a stock and stored in the refrigerator. Prepare the check as you would a sample by making a 1:10 dilution in MPA. This dilution will be used throughout the analyzes. Transfer into a capped storage vial.

25. The water is analyzed as described. Inject into the Al foil boat 250 μL of the dilution, START the 707, on the keypad when ready:

    SAMPLE SIZE 0.250, ENTER
    UNITS g, ENTER

26. Analyze twice, press PRINT, STATISTICS, ENTER. Record the value in the lab notebook, be certain to subtract the blank out. The value should be with in the control limits, record this on the control charts for that quarter. The check must be within the limits.

27. Analysis of the consumer product sample is completed similarly. (See preparation of the samples for analysis.) With the DRIFT OK, inject 250 μL of the dilute sample into the foil boat. There is no change in the operation of the oven with the sample. press START on the 707, PURGE and COND are initiated, when COND=0, on the 720 keypad:

    SAMPLE SIZE 0.250, ENTER
    UNITS g, ENTER

    The boat moves into the oven and the 120 second extraction time starts. The sample is titrated until the stop criteria and the display will read:

    WATER XX.XX%

28. Analysis of the sample is done twice. When completed on the 720 keypad press

    PRINT, STATISTICS, ENTER.
    Record in the lab notebook.

29. At the completion of the analysis, rerun the water control check. This must be within the control limits.

30. If there is any problem with a sample or there is a large discrepancy with the GC results, run the sample by direct injection.

********* NOTES **********

1. Before injecting into the foil, vortex/shake the sample to obtain a homogeneous mix.

2. For samples that have suspended or insoluble particles use the 250 L pipettor to transfer the sample into the foil, through the cap in the insert tube line on the oven above the boat. DO NOT use the syringe.

3. It is VERY IMPORTANT to wait for the foil to cool down sufficiently, otherwise there is the possibility of sample loss and an inaccurate analysis. The READY light on the 707 will come on when the temperature is ready, however it is a good practice to give it another minute or two.

4. When injecting the sample into the foil, depress the plunger slowly and steadily, DO NOT splash the sample or punch a hole in the foil.

5. The foil can be used repeatedly until a visual check indicates it is too dirty or if the foil is punctured with the syringe.

6. When pressing the keys to initiate the KF titration, press firmly and carefully, too fast and the information will not be accepted.

7. The amount of water in the sample is: $\%H_2O$= [(%water in dilution- %MPA blank)/ weight sample,g] X 10

8. In some samples the $\%H_2O$ will be less than or close to that of the MPA blank, in this situation the sample can be run as an aliquot of the original. Using the syringe or a pipettor place in the foil 250 μL of the original undiluted sample and analyze as described. Obtain an average of the weight of the 250 μL aliquot, by weighing into a tared weigh boat. The $\%H_2O$ for the product is obtained as:

$$\%H_2O = \{ (\%\text{water}-\%\text{MPA blank}) / \text{weight sample} \} \times 10$$

Water Determination by Karl Fischer

Water in a consumer product is included in the total voc content determined gravimetrically. The percent of water in a product is analyzed by the Karl Fischer method or by gas chromatography. The fraction of water is then subtracted from the total voc content.

The Karl Fischer is a titrimetric analysis. The reagent contains iodine, sulfur dioxide in pyridine (non-pyridine containing reagents are current). The iodine in the presence of water is reduced to colorless hydrogen iodide, with the endpoint being the presence of free I_2. The basic reaction of the KF reagent with water is:

$$H_2O + SO_2 + I_2 \rightarrow 2HI + SO_3$$
$$SO_3 + R\text{-}OH \rightarrow HSO_4\text{-}R$$

The methanol in the solution drives the equation to the right removing sulfur trioxide.

SOP REVISION HISTORY

1. October 11, 1996: Clarification of QC and addition of the Trip sample.

2. March 10, 1998: Adjusted document font to Times New Roman 12. Inserted appendix A formerly a stand-alone document.